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TECHNICAL REPORT

REACTIONS OF ATOMIC OXYGEN WITH ACETYLENE (I)

KINETICS AND MECHANISMS

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J. V. Michael, and H. Niki

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Harvard University

Cambridge, Massachusetts

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ABSTRACT

The room temperature reaction of acetylene with atomic oxygen has been studied in a moderately fast flow system. The course of the reaction was followed using both the Bendix T.O.F. Mass Spectrometer and a photometric method. The major products of the reaction were carbon monoxide and hydrogen. Large amounts of atomic hydrogen were also observed.

The following reaction scheme is consistent with our results :

1. $C_2H_2 + O \longrightarrow [C_2H_2O^*] \longrightarrow CH_2 + CO$
2. $CH_2 + O \longrightarrow HCO + H$
3. $CH_2 + O \longrightarrow H_2 + CO$
4. $HCO + H \longrightarrow H_2 + CO$
5. $HCO + O \longrightarrow OH + CO$
6. $HCO + O \longrightarrow H + CO_2$
7. $OH + O \longrightarrow H + O_2$

The rate of the overall reaction is determined by the first initial step in which atomic oxygen adds to acetylene to yield an excited complex which then undergoes unimolecular decomposition to give triplet methylene. The rate constant for this initial reaction was measured, at room temperature, as $(8.9 \pm 2.8) \times 10^{-14}$ cc. molecules.$^{-1}$ sec.$^{-1}$. The activation energy was less than 1 kcal. mole.$^{-1}$

Experiments with acetylene-d_2 have established that Reactions (2) and (4) constitute the major pathway by which triplet methylene, produced in Reaction (1), is consumed.

REACTIONS OF ATOMIC OXYGEN WITH ACETYLENE (I)
KINETICS AND MECHANISMS

Introduction

The high temperature oxidation of acetylene has been studied extensively in both flames[1,2,3] and in shock tubes.[4,5]

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1. C.P. Fenimore and G.W. Jones, J. Chem. Phys., 39, 1514 (1963).
2. K.H. Homann, M. Mochizuki and H.Gr. Wagner, Z. phys. Chem. N.F. 37, 299 (1963).
3. R.M. Fristrom, W.H. Avery and C. Grunfelder, 7th Symposium (International) on Combustion, London and Oxford Univ., 1958, 304 (1959).
4. J.N. Bradley and G.B. Kistiakowsky, J. Chem. Phys., 35, 264 (1961).
5. G.P. Glass, G.B. Kistiakowsky, J.V. Michael and H. Niki, J. Chem. Phys., 42, 608 (1965).

An important step in the proposed mechanism of the oxidation is the reaction, $O + C_2H_2$ = Products. However, there is disagreement on the detailed mechanism of this reaction. An abstraction reaction, $O + C_2H_2 = OH + C_2H$, was postulated by Kistiakowsky et al,[4,5] while Fenimore and Jones[1] preferred a mechanism in which the oxygen atom directly attacked the carbon atom of the acetylene. The latter authors proposed a reaction, $O + C_2H_2 = (C_2H_2O) = CH_2 + CO$ or $H + HC_2O$. Furthermore, they deduced the rate constant for the reaction to be $2\text{-}3 \times 10^{-11}$ cc molec^{-1}sec^{-1} between 1200° to 1500°K. In Kistiakowsky's experiments, however, the rate constant was not directly measured. All that could be stated with certainty concerning this reaction was that the rate constant had to be much greater than the rate constant for the reaction, $H + O_2 = OH + O$. The latter reaction has a rate constant at 1500°K of 2×10^{-12} cc molec^{-1} sec^{-1}.[6]

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6. G.L. Schott and J.L. Kinsey, J. Chem. Phys., 29, 1177 (1958).

The present paper describes some experiments which were made at room temperature in a moderately fast flow system[7] in which oxygen atoms were created in the absence of molecular oxygen. The isolated reaction of oxygen atoms with acetylene was studied using mass-spectrometric and photometric techniques.

7. F. Kaufman, Progress in Reaction Kinetics., Vol. 1, P. 1, Pergamon Press, New York (1961).

Experimental

The reactions were observed in the glass flow system shown in Fig. 1. Before each set of experiments the interior of the reaction vessel was either rinsed with 10 % aq. HF or coated with syrupy phosphoric acid to minimize heterogeneous recombination of atoms. The flat quartz window was then attached to the reactor with sealing wax.

Nitrogen was admitted to the flow system through a needle valve, and its flow rate was measured using either a capillary or ball type flowmeter. The nitrogen was partly dissociated by subjecting it to an electrodeless microwave discharge.[8]

8. H.P. Broida and M.W. Chapman, Anal. Chem., 30, 2049 (1958).

The fractional dissociation could be varied continuously from zero to about 1-2% at constant total nitrogen flow rate by using a bypass and valves to control the fraction of the nitrogen flow which passed through the discharge. Ground state oxygen atoms were produced by titrating the nitrogen atoms with nitric oxide.[9,10]

9. G.B. Kistiakowsky and G.G. Volpi, J. Chem. Phys., 27, 1141 (1957).

10. F. Kaufman, J. Chem. Phys., 28, 992 (1958).

Acetylene was admitted to the reactor through a moveable 3 mm OD glass tube.

The progress of the reaction was usually followed mass spectrometrically (cf. Fig. 1(a)). The gas was sampled through a pinhole in either a Teflon or glass wall at the end of the reaction tube. Both a Bendix Time-of-Flight mass spectrometer and a conventional 60° sector magnetic deflection instrument were used to observe the reaction. Both spectrometers have been described elsewhere.[5,11]

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11. J. Berkowitz, W.A. Chupka and G.B. Kistiakowsky, J. Chem. Phys., 25, 457 (1956).

Two changes were made in the T.O.F. spectrometer to observe the neutral species in this reaction. A grid, to which a positive potential of a few volts was applied, was mounted directly behind the pinhole in order to prevent chemi-ions, which are formed in the oxidation,[12] from entering the instrument.

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12. A. Fontijn and G.L. Baughman, J. Chem. Phys., 38, 1784 (1963).

The chemi-ion spectrum and the random chemi-ion noise were thus eliminated. Also, the instrument was operated in the integrating mode, i.e. the single sweep spectra were fed into an electrometer amplifier (the Bendix Analog system). The output from this system was displayed on a Brown potentiometric pen recorder.

In some experiments the chemiluminescence of the reaction[13] was observed (Fig. 1(b)). Light emitted perpendicular to the axis of the flow tube passed through the quartz window and

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13. H.P. Broida and S.L.N.G. Krishnamachari, J. Chem. Phys., 34, 1709 (1960).

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was focused onto the entrance slit of a Jarrell-Ash, 0.5 meter, Ebert mounted plane-grating spectrometer. Light emerging from the exit slit was detected with an RCA 1P28 multiplier phototube operating at 100 volts/stage and cooled with dry ice. The output of the phototube was amplified by a Keithley 610A electrometer and displayed on a Brown potentiometric pen recorder.

AIRCO prepurified nitrogen was used without further purification. Acetylene and nitric oxide obtained from the Matheson Co. were purified by taking either the middle or top fraction in a single bulb-to-bulb distillation. The flow rates of acetylene and nitric oxide were controlled with needle valves and were determined directly by timing a measured pressure drop in a known volume. The initial oxygen atom concentration was calculated from the flow rate of nitric oxide required to titrate the nitrogen atoms. In the experiments at low temperature the relative oxygen atom concentrations were determined photometrically by the addition of a known amount of nitric oxide to the flow tube at a point just upstream of the quartz window. The intensity of the greenish, air after-glow is proportional to the atomic oxygen concentration.[14,15]

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14. F. Kaufman, Proc. Roy. Soc., A247, 123 (1958).
15. M.A.A. Clyne and B.A. Trush, Proc. Roy. Soc., A269, 404 (1962).

The pressure in the flow system was measured using either a tilting Mc Leod gauge or a Wallace & Tiernan 0-20 mm Hg differential pressure gauge. Under typical experimental conditions, i.e. 2 mm Hg pressure and a linear flow speed of 250-500 cm sec^{-1}, corrections for radial concentration gradients, back diffusion and viscous pressure drop were negligible.[7] However, rate of diffusion of atomic hydrogen is extremely great and under the conditions of these experiments corrections for back diffusion of this species are necessary.

Results

The reaction of oxygen atoms with acetylene is first order in both reactants. The rate of the reaction is given by the expression :

$$-n\frac{d(C_2H_2)}{dt} = -\frac{d(O)}{dt} = k_1 (C_2H_2)(O) \qquad (A)$$

where k_1 is the rate constant for the reaction, $O + C_2H_2 = Products.$, n was determined from the stoichiometry of the reaction and was found to be approximately 2.

In the presence of large excess of atomic oxygen, the atomic oxygen concentration will remain almost constant throughout the reaction and Eq.(A) integrates to $\ln \frac{(C_2H_2)}{(C_2H_2)_o} = -\frac{k_1}{n}(O)_o t$, where the subscript o refers to the initial pre-reaction concentrations. Similarly in the presence of a large excess of acetylene, one obtains $\ln \frac{(O)}{(O)_o} = -k_1(C_2H_2)_o t$. It should be noted that if the initial ratio of reactants is not the exact stoichiometric ratio, as reaction proceeds the ratio of reactants remaining will change away from stoichiometric so that one reactant will eventually be in large excess.

The pseudo first order behavior of the system is demonstrated in Figs. (2b) and (3), which show the exponential decay of oxygen atoms in an acetylene rich mixture and of acetylene in an oxygen atom rich mixture, respectively. In these experiments, the relative concentrations of reactants were measured using the T.O.F. mass spectrometer. The initial non-linear portion of Fig.(2b) is caused by incomplete mixing of the reactants. Fig.(2a) shows the behavior of the acetylene concentration at the pinhole as a function of the distance between the pinhole and the acetylene inlet in the absence of atomic oxygen. As can be seen, mixing is completed at about 2 cm from the inlet. The validity of the assumption that the atomic oxygen concentration does not vary with time in these very oxygen atom rich mixtures was confirmed by direct observation of the atomic oxygen concentration using the T.O.F. mass spectrometer.

The distance, d, between the acetylene inlet and the pin-hole of the mass spectrometer is related to the time, t, before observation by the relation, $d = t\,v$, where v is the linear flow speed in the reactor.

Table 1 shows the rate constant k_1 calculated from a number of experiments similar to those shown in Figs. (2) and (3). A number of experiments in which the $CH(A^2\Delta - X^2\pi)$ chemiluminescence was monitored as a function of the reaction time is included in the table. These are included since it was found especially easy to vary the temperatures of the reaction in the apparatus, Fig. 1(b), in which the chemiluminescence was observed. In oxygen atom rich mixtures the intensity of CH* radiation is proportional to the cube of acetylene concentration, and was found to be almost independent of temperature.[16]

16. Part (II) of the paper, to be published in this journal.

Thus the slope of the $\ln(CH^*)$ vs t plot is three times that of $\ln(C_2H_2)$ vs t.

The average value of the rate constant, k_1, calculated from Table 1 is $(8.9 \pm 2.8) \times 10^{-14}$ cc molec^{-1} sec^{-1}. It was calculated that the diffusion of oxygen atoms lowers the measured rate constant 5% below its real value. However, no correction was made to the measured values since greater uncertainty arises in the measurement of the atomic oxygen concentration. Small deviations were noticed in k_1 as measured by the three apparatuses. These differences can be attributed largely to the use of different flow meters and to errors in the measurement of the dimensions of the apparatus from which the linear flow speed is calculated. The rate constant, k_1, is independent of total pressure of inert gas in the system as can be seen from Table 1. The measurements at 0.9 mm and at 8 mm Hg pressure, which gave similar values of k_1, were carried out within a few minutes of one another. Only the flow rate of nitrogen was varied between these measurements and an absolute calibration of the flow meter was made shortly afterwards at the two settings.

In order to determine the apparent activation energy of the reaction, experiments were made in which the flow tube was surrounded by dry ice. At the pressures of these experiments the gases should then be equilibrated to the wall temperature within one centimeter ; (Average diffusion time to the wall is 2×10^{-3} sec., v = 250 cm sec^{-1}, and tube diameter is 16 mm.) The temperature at the center of the flow tube was calculated roughly by assuming that all the heat of the reaction, $C_2H_2 + 2\ O = 2\ CO + H_2$, was liberated at a distance from the wall equal to one third of the tube diameter. The temperature was estimated to be less than 40°C above the wall temperature — a result in agreement with that measured by Fontijn et al[17] for a reaction vessel of different diameter.

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17. A. Fontijn, J.M. Hogan, and W.M. Miller, 10th Symposium (International) on Combustion, Cambridge, England (1964).

Using a large excess of oxygen atoms the rate constant for the reaction was measured by monitoring the intensity of $CH(A^2\Delta \rightarrow X^2\pi)$ chemiluminescence as a function of distance from the acetylene inlet. The apparatus was then allowed to return to room temperature and the measurements were repeated using the same flow conditions. A correction was made for the change in linear flow speed with temperature and for the change in initial oxygen atom concentrations. The relative oxygen atom concentrations were measured at the two temperatures using the nitric oxide photometric technique.[13] The results of these measurements may be seen in Table 1 (c) and (d) . The reaction shows little, if any, apparent activation energy.

The stoichiometry of the reaction was measured by three different techniques. Using the T.O.F. mass spectrometer the amount of acetylene remaining unreacted in an acetylene rich mixture was measured at a point far enough downstream from the acetylene inlet, 20 cm, so that no detectable concentration of oxygen atoms remained. From this measurement it was calculated that one molecule of acetylene is oxidized by every 2.1 oxygen atoms.

Another experiment was performed in which sufficient acetylene was added to the oxygen atom stream to make the acetylene peak at m/e = 26 just detectable at 20 cm from the acetylene inlet. The area under the oxygen atom peak at m/e = 16 was then measured and remeasured in the absence of acetylene. The number of oxygen atoms that were removed by one molecule of acetylene in this experiment was calculated to be 1.6. Finally in another apparatus the oxygen atoms were monitored photometrically by addition of nitric oxide. The amount of acetylene required just to extinguish the green air-afterglow at a point well downstream of the reaction was measured. From this measurement and a knowledge of the initial oxygen atom concentration, the number of oxygen atoms removed by each acetylene molecule was calculated to be 2.0. Indirect evidence that each molecule removes approximately two oxygen atoms was provided by the observation that a linear second order kinetic plot of $(C_2H_2)^{-1}$ vs t could be obtained when using an initial oxygen atom concentration equal to 2.3 that of the initial acetylene concentration.

The main products of the reaction, in the absence of molecular oxygen, were carbon monoxide and hydrogen. Hydrogen atoms were also formed in sizeable concentrations. An accurate quantitative estimate of the yield of carbon monoxide was difficult to obtain using the mass spectrometer since carbon monoxide was observed as a small addition to the already large mass peak at m/e = 28, caused by molecular nitrogen. However, a crude estimate that in oxygen atom rich mixtures 1.5 ± 0.5 molecule of carbon monoxide are formed for every molecule of acetylene oxidized was obtained in experiments using 10 to 1 helium to nitrogen mixtures as carrier. When such a mixture passes through the discharge a larger pe-rcentage dissociation of nitrogen occurs than when pure nitrogen is used. Thus the molar ratio of carbon monoxide, formed in the reaction, to background nitrogen is increased. 0.8 molecule of hydrogen was observed for every molecule of acetylene oxidized.

In an attempt to characterize the reactions leading to the formation of molecular and atomic hydrogen, a study was made of the yields of these two products as a function of initial acetylene concentration and the time of reaction. Fig. 4 shows the time dependence of H_2 and H concentrations at a given acetylene concentrations. Since mixing was not complete for about four milliseconds, (d= 2 cm), the initial rates of production could not be obtained and these are only implied by the dotted lines in this figure. Comparison of the concentration of acetylene reacted shows a striking similarity indicating that H_2 is formed at about the same rate that acetylene is consumed. Over the range of time available for observation the H atom concentration is essentially constant within experimental error. This behavior of H atom concentration was found to hold over a wide range of acetylene concentrations.

In experiments carried out at a fixed time, i.e. d = constant, but in which the initial concentration of acetylene was varied, the concentration of H_2 produced in the reaction was linear as a function of the initial acetylene concentration. However, as the acetylene concentration approached one-half the oxygen atom concentration, i.e. stoichiometric mixture, a slight downward bending in the curve of H_2 vs flow rate of acetylene was noted. The H atom concentration is insensitive within experimental error to initial acetylene concentration.

Water and carbon dioxide were formed only in small quantities, their molar concentration amounting to about only 3-5% of that of the reactants consumed. However, in acetylene rich mixtures other products were also observed (Table 2). They were identified by making experiments with acetylene-d_2 and their approximate abundances were calculated using the assumption that their ionization cross sections are equal to that of acetylene at 20 eV. The mass peaks at m/e = 39, 40, and 42 increased slightly as a function of reaction time, while that at m/e = 50 decayed exponentially with time in a manner similar to that of oxygen atoms.

A search was made for CH_2 radical at m/e = 14, but it was unsuccessful. However, in the reaction of oxygen atoms with methyl acetylene, the next member of the acetylenic series, large amounts of acetylene were observed as an intermediate in the oxidation. The observed concentration of acetylene was approximately 0.3 of that of the methyl acetylene consumed in the reaction.

In order to determine the origin of some of the products of the reaction some experiments were performed using isotopically labelled compounds. In one experiment, an equimolar mixture of acetylene and acetylene-d_2 was oxidized, and the isotopic distribution of molecular hydrogen, which was formed in the reaction, was measured. The peak at m/e = 3 was always twice as large as that at m/e = 4, even at the shortest reaction times that were observed. The peak at m/e = 2 was disregarded since it was composed of contributions from both H_2 and D atoms. The sensitivity of the mass spectrometer to HD was never measured but its sensitivity to H_2 was 2.2 times that towards D_2 probably due mainly to more rapid diffusion of H_2 through the pin-hole. From these results it is obvious that the isotopic distribution in molecular hydrogen was mainly, if not completely, random. In these experiments it was noted that no C_2HD was formed and thus no isotopic scrambling of the initial acetylene occurred. When $^{18}O_2$ was added to the $C_2H_2 - {}^{16}O$ reaction, much of the carbon dioxide observed was of the form of $C^{18}O^{18}O$. At the time this suggested that carbon dioxide was being formed principally from reactions of molecular oxygen and thus some experiments were made in which the concentration of carbon dioxide observed well downstream of the reaction, 20 cm, was monitored as a function of added molecular oxygen. The results are shown in Table 3.

Discussion

The first order dependence of the rate of the reaction on both acetylene and atomic oxygen concentration show that the initial reaction $C_2H_2 + O \longrightarrow$ Products, is rate controlling in this system. The magnitude of the rate constant, which is similar to that of the well-known addition reaction of atomic oxygen with ethylene[18], its lack of temperature dependence and the observation of the adduct C_2H_2O in small quantities, all strongly indicate that in the initial reaction addition occurs to form C_2H_2O. The abstraction reaction $C_2H_2 + O \longrightarrow C_2H + OH$ is ruled out by the lack of water as a major product and by the extremely small activation energy of the reaction.

18. R.J. Cvetanović, J. Chem. Phys., 30, 19 (1959).

The addition complex C_2H_2O can undergo three types of reaction : a unimolecular decomposition may occur; it may take part in a bimolecular reaction with O atoms or acetylene; or the complex may be collisionally stabilized before further reaction occurs. If the bimolecular reaction with O atoms occurs,

$$C_2H_2 + O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_2H_2O \qquad (1)$$

$$C_2H_2O + O \xrightarrow{k_2} \text{Products} \qquad (2)$$

then the rate of the reaction is given by the expression,

$$-2\frac{d(O)}{dt} = -\frac{d(C_2H_2)}{dt} = \frac{k_1k_2(O)^2(C_2H_2)}{k_{-1} + k_2(O)} \qquad (B)$$

Now k_{-1} cannot be greater than $k_2(0)$ since the rate would then be dependent on the square of the oxygen atom concentration. However, for $k_2(0)$ to be greater than k_{-1}, the lifetime of addition complex would have to be of the order of 10^{-5} sec., since the partial pressure of O atoms in these experiments was about 10^{-2} mm Hg. This is very unlikely since the lifetime of a five atom complex containing considerably more than the minimum activation energy with respect to a unimolecular decomposition, is usually less than 10^{-8} sec.[19]

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19. See, for example, D.W. Setser and B.S. Rabinovitch, Can. J. Chem. 40, 1425 (1962).

The pressure independence of the rate constant suggests either that the collisional deactivation of the complex occurs very efficiently at all pressures between 0.9 to 9 mm Hg, or that the complex undergoes a rapid unimolecular decomposition. The former case is very unlikely since it implies a life time of at least 5×10^{-7} sec for the complex. Thus we conclude that the adduct undergoes unimolecular decomposition. If one assumes that the stable compound C_2H_2O which was observed in about 1% yield in acetylene rich mixtures, arises by stabilisation of the complex by molecular nitrogen and that this stabilisation occurs on almost every collision, one can calculate the lifetime of the complex to be $\sim 10^{-9}$ sec.

From thermochemical considerations the most probable products of the decomposition of the complex are either methylene or ketyl radicals, i.e., $C_2H_2O \longrightarrow CH_2 + CO$ or $HC_2O + H$. In order for spin multiplicity to be conserved in this reaction, the methylene produced would have to be in a triplet state. Several pieces of evidence favor the decomposition yielding triplet methylene radicals. The presence is supported by the detection of C_3H_4 in acetylene rich mixtures. This molecule probably arises from an addition

reaction of triplet methylene to acetylene. The analogous reaction of singlet methylene radicals gives rise to a "hot" cyclopropene molecule which in turn rearranges, at low pressures, to give allene and methyl acetylene[20], $CH_2 + C_2H_2 \longrightarrow (\text{△}^*) \longrightarrow C_3H_4$.

20. H.M. Frey, Chem. and Ind. (London)., 1266 (1960).

The mass peak at m/e = 39 (C_3H_3) probably arises mainly as a cracking pattern from C_3H_4. However, the ratio of mass peaks at m/e = 40 and 39 varied slightly with stoichiometry and thus some free C_3H_3 radicals may also be present. The presence of methylene is also suggested by the pattern of the chemi-ion spectra observed in this reaction, since many of the abundant chemi-ions were observed to be 14 mass unit apart.[16] The addition reactions of triplet methylene are well known.[21]

21. F.J. Duncan and R.J. Cvetanovic, J. Am. Chem. Soc., 84, 3595 (1962).

Triplet methylene might be expected to react very rapidly with ^3P oxygen atoms. Thus, our failure to observe methylene with the mass spectrometer is not unexpected since its concentration must be very small. In the analogous reaction of O atoms with methyl acetylene large amounts of acetylene were observed early in the reaction. Hot triplet ethylidene radicals, which are formed by the reaction analogous to the formation of triplet methylene namely, $CH_3-C\equiv CH + O \longrightarrow (CH_3-CH-CO) \longrightarrow CH_3-CH: + CO$, probably decompose at these low pressures to give acetylene, in a similar manner to the hot ethylidene radicals produced in the photolysis of methyl ketene[22] and diazoethane.[23] The multiplicity of these latter radicals is unknown. Thus the formation of large amounts of

acetylene in the reaction of methyl acetylene with atomic oxygen is strong evidence for the reaction scheme proposed.

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22. D.P. Chong and G.B. Kistiakowsky, J. Phys. Chem., 68, 1793 (1964).
23. H.M. Frey, J. Chem. Soc., 2293 (1962).

From the stoichiometry of the reaction it is obvious that triplet methylene must react rapidly with atomic oxygen. The products of the reaction are carbon monoxide and hydrogen, which are formed as rapidly as acetylene is oxidized, and atomic hydrogen. A possible mechanism including the initial reaction is :

$$C_2H_2 + O \longrightarrow CH_2 + CO \qquad (1)$$

$$CH_2 + O \longrightarrow HCO + H \qquad (2)$$

$$CH_2 + O \longrightarrow H_2 + CO \qquad (3)$$

$$H + HCO \longrightarrow H_2 + CO \qquad (4)$$

$$O + HCO \longrightarrow OH + CO \qquad (5)$$

$$O + HCO \longrightarrow H + CO_2 \qquad (6)$$

$$OH + O \longrightarrow H + O_2 \qquad (7)$$

The fact that H_2, HD, and D_2 are formed in statistically random amounts in the oxidation of an equimolar mixture of C_2H_2 and C_2D_2 imples that reaction (2) must proceed much more rapidly than reaction (3), since the isotopic exchange reaction of molecular hydrogen :

$$H + D_2 \longrightarrow HD + H \qquad (8)$$

is extremely slow at room temperature[24] and since no isotopic exchange in the acetylene was observed.

24. H.W. Melville and J.C. Robb, Proc. Roy. Soc., A 196, 445 (1949)..

The observation of the hydrocarbon flame bands, emitted by HCO, in the low pressure reaction of atomic oxygen with acetylene[25] suggests that HCO may be an important intermediate species in this reaction. Reaction(2) provides a

25. W.M. Vaidya, Proc. Roy. Soc., A 279, 572 (1964).

possible mechanism for its formation. Indeed since this reaction is very exothermic the HCO may well be formed in an excited state.

Carbon dioxide, water and molecular oxygen , the products of reaction(5) and subsequent reactions, are formed only in very small quantities in the reaction and thus reaction(4) must be the major pathway for the removal of HCO. This is in agreement with the observation that only two oxygen atoms are removed for every molecule of acetylene oxidized, for at least three oxygen atoms would be removed if reaction(5) were of major importance. Reaction(4) also provides a mechanism for the rapid production of molecular hydrogen.

The experimental observation that the atomic hydrogen concentration did not vary during the time in which the reaction was observed indicates that a delicate balance between formation and removal of H atoms must exist. Since the mechanism suggests that H atoms are formed as rapidly as acetylene is oxidized, an equally rapid reaction removing H atoms must occur. The rate of the acetylene catalysed recombination of H atoms has been measured by Dingle and LeRoy.[26]

26. J.R. Dingle and D.J. LeRoy, J. Chem. Phys., 18, 1632 (1950).

They found the reaction to be first order in both acetylene and atomic hydrogen concentration and to have a rate constant 1.3×10^{-14} cc molec^{-1} sec^{-1}. Thus in our system the rate of acetylene catalysed recombination of hydrogen atoms is much faster than either wall recombination[27] or third order volume recombination.[28] However even the acetylene catalysed re-

27. W.R. Schulz and D.J. LeRoy, Can. J. Chem., 40, 2413 (1962).
28. See for example: H. Wise and C.M. Ablow, J. Chem. Phys., 35, 10 (1961).

combination does not remove H atoms nearly as fast as they are formed from oxidation of acetylene, and thus reaction(4) must be the major route by which H atoms are removed and molecular hydrogen is formed.

The results in Table 3 clearly show that carbon dioxide is not formed mainly by a reaction of molecular oxygen. The results of the experiments made with $^{18}O_2$ were found to be inconclusive since the reaction

$$^{16}O + {}^{18}O{}^{18}O \longrightarrow {}^{16}O{}^{18}O + {}^{16}O$$

has recently been shown to occur extremely rapidly with a bimolecular rate constant $1.7 \times 10^{-(12 \pm 0.2)}$ cc molec^{-1}sec^{-1}.[29]

29. W. Brennen and H. Niki, to be published in J. Chem. Phys.

It is impossible to say whether the small amount of carbon dioxide formed in this system arises from secondary oxidation of carbon monoxide or from some other source.

One product that is formed in small quantities in acetylene rich mixtures is diacetylene. It probably arises from the reaction,[4] $C_2H + C_2H_2 \longrightarrow C_4H_2 + H$. However, whether the small amount of C_2H formed comes from a small contribution of the abstraction reaction, $C_2H_2 + O \longrightarrow C_2H + OH$, or via a more complex pathway is impossible to state.

Thus to summarize, it may be concluded that oxygen atoms react with acetylene at room temperature mainly via reaction (1). The rate constant, k_1, for the primary reaction is $(8.9 \pm 2.8) \times 10^{-14}$ cc molec^{-1}sec^{-1} and the reaction has little, if any, activation energy. The subsequent reactions which yield the stable products are much faster than the initial reaction and are therefore difficult to characterize.
A mechanism which is both reasonable and in agreement with experimental results has been presented.

It is clear that the initial reaction which occurs between oxygen atoms and acetylene at room temperature is much too slow to be the one postulated by Kistiakowsky and observed by Fenimore and Jones in the high temperature oxidation of acetylene, and thus, oxygen atoms must react with acetylene by way of another mechanism at high temperatures.

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Table 1

RATE CONSTANTS FOR REACTION O + C_2H_2

Species undergoing 1st order decay	(N_2) x 10^{-16} molec/cc	$(O)_o$ x 10^{-14} molec/cc	$(C_2H_2)_o$ x 10^{-14} molec/cc	k_1 x 10^{14} molec/cc sec
O atom	5.40	8.53	19.8	7.2[a]
C_2H_2	5.40	5.8	2.7	14
"	5.40	5.8	1.1	13
CH^* chemiluminescence	6.9	4.7	10.7	6.9[b]
"	6.9	10.0	1	6.6
"	4.8	10.0	2.15	5.9
"	4.5	8.6	2.9	8.0
"	7.6	4.0	1.7	9.0[c]
"	5.1	6.1	1.2	10[d]
"	2.7	4.7	1	7.1
"	24.0	4.7	1	9.0

Experiments were performed at room temperature unless otherwise specified.

$$k_1 = (8.9 \pm 2.8) \times 10^{-14} \text{ cc molec}^{-1} \text{ sec}^{-1}$$

a. This value was calculated assuming n = 2 in Eq.(A).

b. The determinations of k_1 made from measurements on chemiluminescence have been corrected assuming $(CH^*) \propto (C_2H_2)^3(O)^2$

c. Measured at 195°K.

d. Measured at 295°K immediately after the measurement at 195°K.

Table 2.

ABUNDANCE OF MINOR SPECIES OBSERVED

Mass Peak (m/e)	Species	Molar Abundance (%)*
39	C_3H_3	1.5
40	C_3H_4	3.0
42	C_2H_2O	1.0
50	C_4H_2	2.0

* As compared with amount of acetylene oxidized.

Table 3

EFFECT OF ADDED O_2 ON CO_2 FORMATION*

$(CO_2) \times 10^{-13}$ molec cc^{-1}	$(O_2) \times 10^{-14}$ molec cc^{-1}
1.4	1.3**
1.5	8.5
2.0	20
2.4	47
3.6	78
3.9	80

* (CO_2) measured at 10 cm downstream from acetylene inlet. $v = 660$ cm sec^{-1}, $P_{total} = 0.9$ mm Hg, $(N_2) = 2.7 \times 10^{16}$ molec cc^{-1}, $(O)_o = 3.6 \times 10^{14}$ molec cc^{-1}, and $(C_2H_2)_o = 2.0 \times 10^{14}$ molec cc^{-1}.

** No O_2 added.

Figure Captions

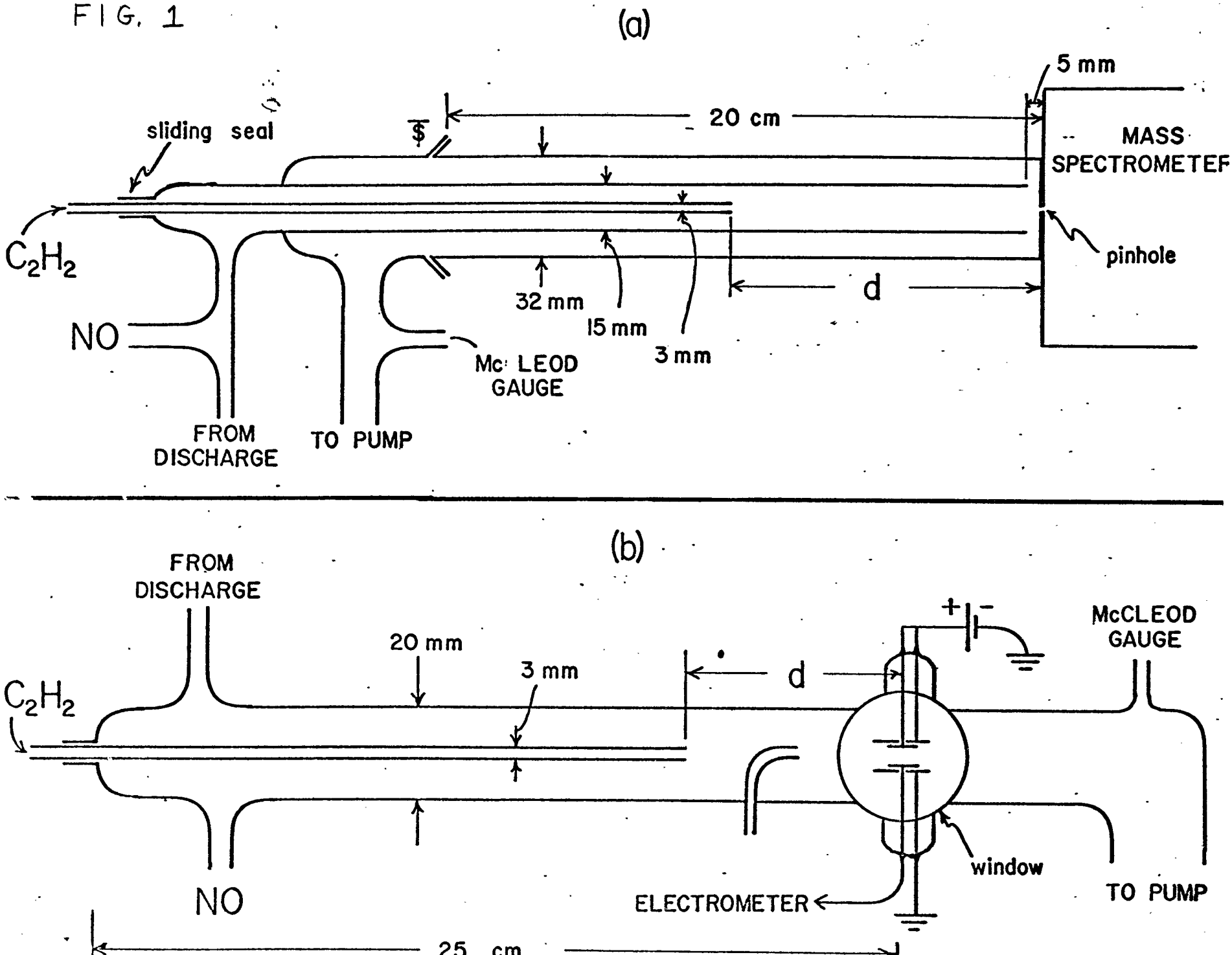
Fig. 1., Schematic diagram of the apparatus.
- a) Mass Spectrometric observation.
- b) Observation of Chemiluminescence.

Fig. 2., The concentration of acetylene as a function of the distance between the acetylene inlet and the pinhole.
- a) In the absence of atomic oxygen.
- b) During the reaction of an oxygen rich mixture:
  $(N_2) = 5.47 \times 10^{16}$ molec. $cc.^{-1}$
  $(O)_o = 3.42 \times 10^{14}$ molec. $cc.^{-1}$

Fig. 3., The concentration of atomic oxygen as a function of the distance between the acetylene inlet and the pinhole during the reaction of an acetylene rich mixture :
$(N_2) = 5.47 \times 10^{16}$ molec. $cc.^{-1}$
$(C_2H_2) = 2.12 \times 10^{15}$ molec. $cc.^{-1}$

Fig. 4., A plot of m/e = 2 amd m/e = 1 as a function of reaction time in the reaction of atomic oxygen with acetylene : $(C_2H_2)_o \simeq (O)_o$

FIG. 1


(a)
5 mm
20 cm
sliding seal
MASS SPECTROMETEF
pinhole
C_2H_2
NO
32 mm
15 mm
3 mm
d
Mc LEOD GAUGE
FROM DISCHARGE
TO PUMP
(b)
FROM DISCHARGE
20 mm
3 mm
d
McCLEOD GAUGE
C_2H_2
NO
window
ELECTROMETER
TO PUMP
25 cm

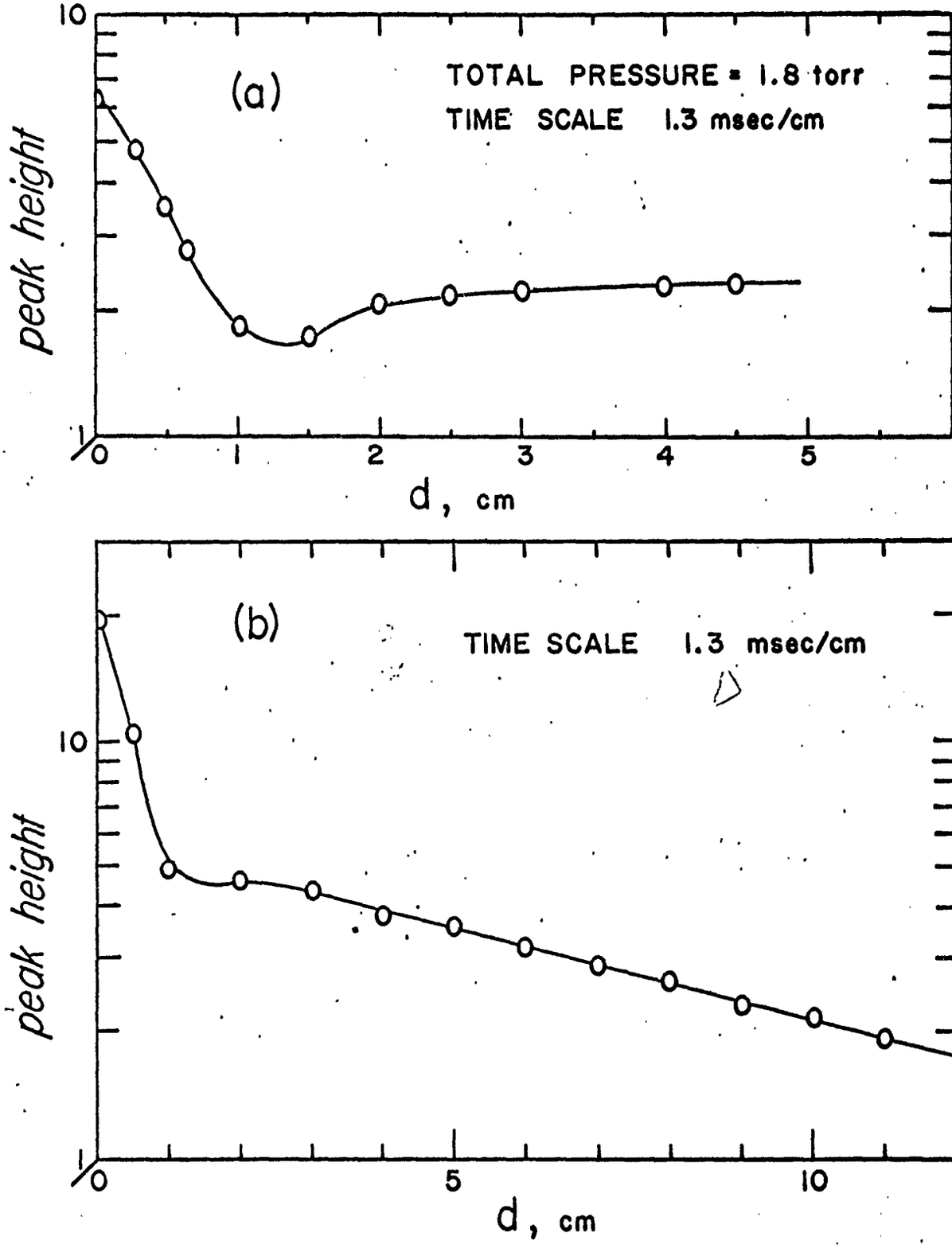

(a)
TOTAL PRESSURE = 1.8 torr
TIME SCALE 1.3 msec/cm
peak height
10
1
0
1
2
3
4
5
d, cm
(b)
TIME SCALE 1.3 msec/cm
peak height
10
1
0
5
10
d, cm

FIG. 2

Fig 2

FIG. 3

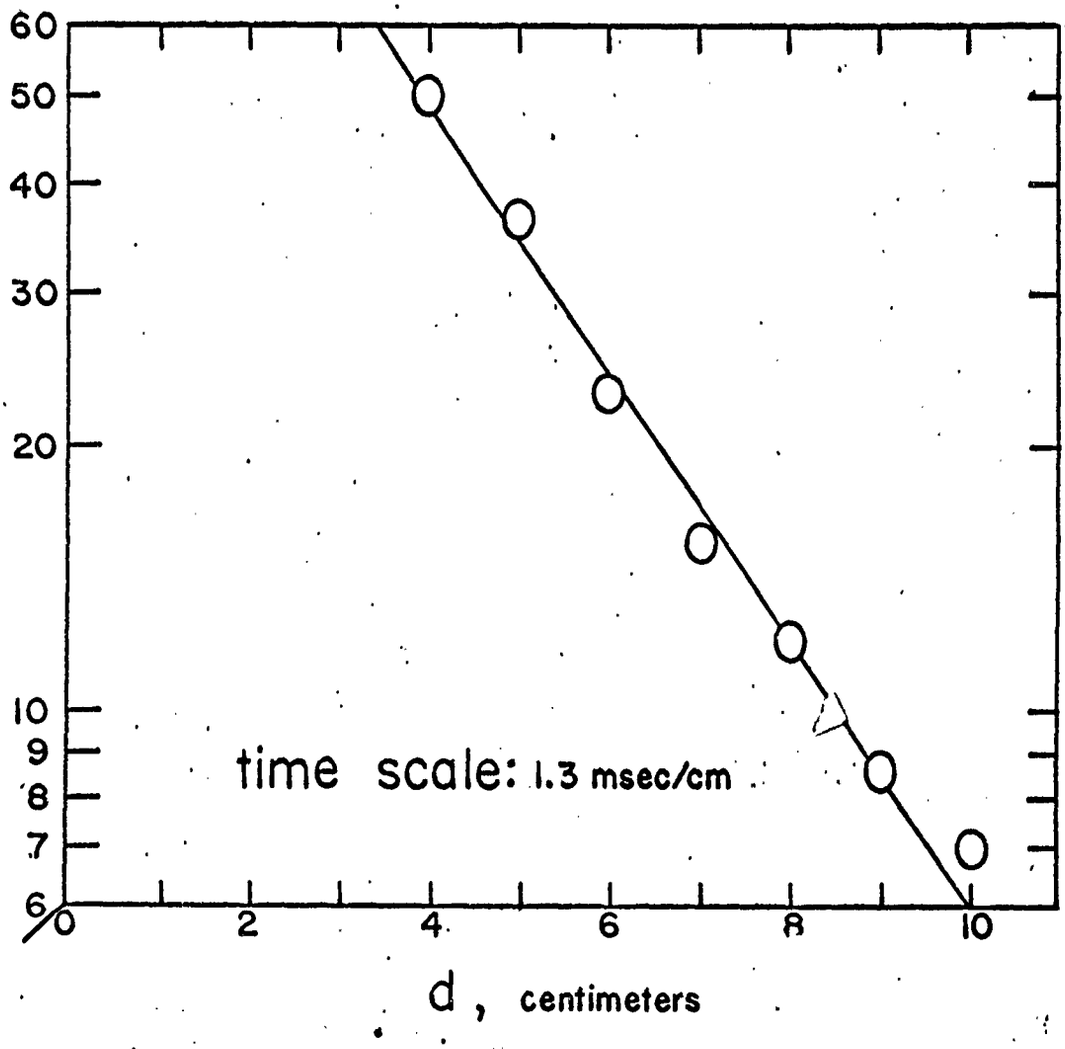

peak height
60
50
40
30
20
10
9
8
7
6
time scale: 1.3 msec/cm
0
2
4
6
8
10
d, centimeters

Fig 3

FIG. 4

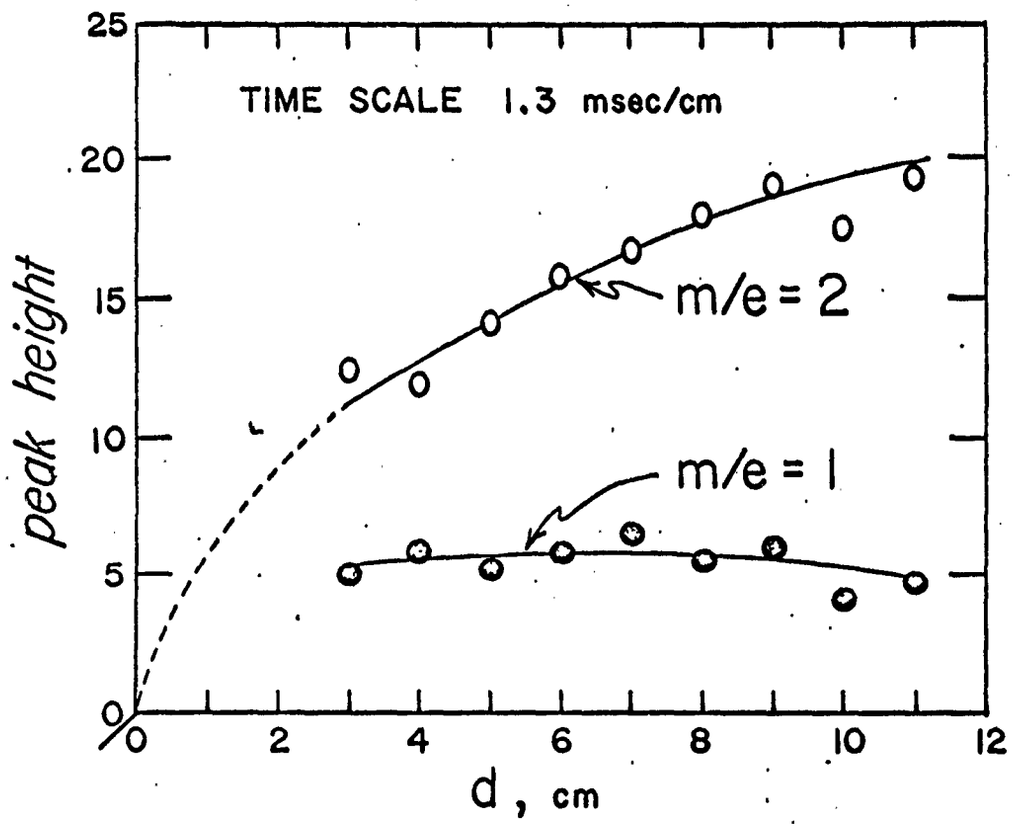

TIME SCALE 1.3 msec/cm
peak height
m/e = 2
m/e = 1
d , cm
0
5
10
15
20
25
0
2
4
6
8
10
12

Fig 4